The compatibility of potential bioderived fuels with Jet A-1 aviation kerosene

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Abstract

Environmental concerns and the rising cost of crude oil have incentivised the search for alternative aviation fuels. However, any potential alternatives must be thoroughly characterised and tested. In this investigation nine potential biofuels derived from sustainable sources were tested for their compatibility with Jet A-1 aviation kerosene. The fuels chosen were n-butanol, n-hexanol, butyl levulinate, butyl butyrate, ethyl octanoate, methyl linolenate, farnesene, ethyl cyclohexane and limonene. Viscosities were determined between -30 and 40 °C and were observed to increase with decreasing temperature roughly in accordance with ideal fluid behaviour. Cloud point temperatures of all samples were tested and all fuels except n-butanol and methyl linolenate were found to be below the specification maximum. Flash points of all fuels apart from pure and blends of ethyl cyclohexane and n-butanol were found to be greater than 38 °C, the minimum threshold specified in the standard. Of all the samples only the hydrocarbon fuels met the required energy content minimum with energy content decreasing with increasing oxygen content. The effect of each fuel on the range vs. the payload, relative to Jet A-1 was determined using a simplified model in order to ascertain likely impact of adoption upon airline operations. Only limonene fulfilled all the requirements of an alternative aviation fuel, though butyl butyrate and ethyl octanoate were acceptable except for the reduced energy density.

Keywords

aviation, biodiesel, biofuel, farnesene, oxygenated fuel

1. Introduction

Compositional changes to the atmosphere due to anthropogenic emissions are acting to shift the complex natural equilibrium of our environment. Globally aviation emissions contribute approximately 2% of all anthropogenic CO_2, however when taking into account enhancements in the radiative forcing originating from species identity and emission altitude sensitivity, this figure rises to around 3.5% of all anthropogenic effects [1, 2]. Economic considerations are also exerting pressure upon the aviation industry with the steady increase in crude oil price and an increasingly restrictive legislative horizon forcing proactive consideration of alternative fuels.

Over the last decade there has been increased interest in the development of biofuels for the aviation sector, leading to various demonstration flights by many major airlines. However, concerns over the compatibility of the fuel with the aircraft operation have limited the development of these fuels to date. An alternative fuel must have a number of characteristics to be considered suitable for aviation. These include the need for a high energy density to maximise range, good atomisation, rapid evaporation, an ability to be relit at altitude though a low explosive risk on the ground, they must have a suitably low viscosity, an extremely low freezing point, good chemical stability, be reasonably non-toxic and be widely available while being economically competitive with current Jet A-1 fuels [3-6]. For this reason only a small selection of alternative fuels are currently available. Arguably Sasol lead the way in the production of novel alternative jet fuels and a Fisher-Tropsh (FT) synthetic jet fuel comprising of 50% Jet A-1 and 50% F-T fuel is now certified under the DEF STAN (91-91) specification [7]. Although the use of F-T fuels could address the security of supply, it does little to contribute towards any positive environmental impact [7]. Emissions associated with F-T fuels' lifecycles are generally considerably higher [8, 9]. A life cycle assessment showed associated GHG emissions for CtL F-T to be 123% that of aviation kerosene, though the use of biomass instead of coal could reduce this figure by as much as 30-80% [7, 10].

An alternative source of fuel is produced via the hydrotreatment of bio-derived esters and fatty acids to produce paraffins, a portion of which are then hydroisomerised (HEFA) [11]. The fuel produced through this process is chemically similar to F-T synthetic jet fuel and like F-T fuels it has a very low aromatic and sulfur content. HEFA was approved for use as a 50% blend with conventional fuel in July 2011. Emissions associated with the production of HEFA from jatropha oil have been calculated to be approximately 45% that of conventional jet fuel from fossil oil [10].

Alternatively a number of potential biofuels, which are chemically dissimilar to aviation kerosene, have been proposed in the academic literature. As most of these fuels have a known chemical structure the properties are constant irrespective of the geographical location, processing or source of biomass feedstock. Pinene derivatives have been suggested as an alternative aviation fuel and more recently as a high density tactical fuel, similar to JP10. This is achieved through isomerisation and dimerization of the pinene [12]. A consequence of dimerising the fuel however, is that the low temperature properties of the

fuel are severely affected. The viscosity of the unblended fuel is also much greater than that required by the aviation fuel specification [13]. The emergence of bioethanol as a road transport fuel has paved the way for consideration of other alcohols as alternative fuels to Jet A-1 [14]. In aviation, the energy content of the fuel is extremely important, and the use of bioethanol is not particularly desirable for this reason. The use of higher alcohols would allow their use without sacrificing so much energy density, as the carbon to oxygen ratios increase with increasing molecular mass. *n*-Butanol, for example, may be obtained through fermentation of lignocellulosic biomass through the Acetone-Butanol-Ethanol (ABE) fermentation pathway [15], whereas the use of modified organisms gives rise to the possibility of producing n-hexanol and higher alcohols [16].

While alcohols can be used as a potential source of fuel, Jenkins *et. al.* demonstrated that butyl butyrate produced via the esterification or oxidation of *n*-butanol is a more promising aviation fuel component, and exhibits suitable low temperature properties [17]. Producing alcohols and esters from fermentation is relatively well understood, though recently a large research effort has been invested in producing hydrocarbons by the same route. Amyris have achieved a fermentation pathway for the production of farnesene, this has been done through utilisation of the mevalonate or deoxyxulose (DXP) pathways to produce farnesyl pyrophosphate which is then converted to farnesene by a sesquiterpene synthase [18]. While not as developed, another promising biofuel through use of metabolically engineered organisms is limonene. Limonene may be produced via the mevalonate and DXP pathways into geranyl pyrophosphate, which is then transformed into pinene and limonene by monoterpene synthases [19]. While yields of these monoterpenes are low, they could prove to be very suitable for aviation, and characterisation of their physical properties in blends with kerosene is necessary to guide further research in this area.

Cycloalkanes are found in fossil oil derived commercial aviation fuels, and to an even greater extent in coal derived alternative fuels such as CtL F-T fuels [20]. It seems likely that a promising alternative for aviation would be based on this structural motif. A promising bioroute to production of these types of compounds would be through the hydrogenation of bio-aromatic compounds, such as phenylalanine or 2-phenylethanol. In both cases it would feasibly form ethyl cyclohexane.

While fermentation offers one route to convert cellulosic biomass, the acid hydrolysis of cellulose can be used to produce levulinic acid, which may then be esterified with bioethanol or biobutanol in order to yield ethyl or butyl levulinate [21]. Miscibility of ethyl levulinate with kerosene is poor, though butyl levulinate seems a promising alternative [17]. While hydroprocessed triglycerides are being accepted as synthetic aviation fuels, a number of studies have shown biodiesel, the fatty acid alkyl esters produced by the transesterification of glycerides, to be a suitable fuel for gas turbine engines [22, 23]. Typically biodiesel contains straight chain fatty acid esters of 16 or 18 carbons in length which can have up to 3 double bonds. However, the melting points of the long chain saturated and monounsaturated esters are too high to be suitable for aviation. Reducing the chain length or increasing the level of polyunsaturation reduces the

freezing point substantially. In this investigation ethyl octanoate (C8:0) and methyl linolenate (C18:3) were investigated as potential aviation substitutes. These esters provide a good model for the behaviour of shorter chain or highly unsaturated biodiesel components.

While these nine components are extremely promising candidates for aviation based on their low temperature properties, further work is needed to establish further key fuel properties and their interaction with jet fuel so as to provide a fuller assessment as to their suitability. Over the course of this study the key fuel properties of the potential biofuels, and their blends, were assessed (table 1). Based on these findings the applicability, and maximum blend level of these fuels was evaluated.

2. Materials and Methods

2.1 Materials

The potential alternative fuels were ethyl cyclohexane (≥99%), (R)-(+)-limonene (≥97%), farnesene (mixture of isomers, containing 0.1% α-tocopherol), butyl levulinate (98%), ethyl octanoate (≥99%), butyl butyrate (≥98%), 1-hexanol (anhydrous, ≥99%), 1-butanol ((≥99.5%)) and methyl linolenate (≥99%). These were supplied by Sigma-Aldrich and used without further purification. Where necessary alternative fuels were refrigerated in order to minimise degradation. The Jet A-1 used in this study was supplied by Air BP and was stored in a sealed 5L steel fuel container at room temperature. The Jet A-1 was fully compatible with the DEF STAN 91-91 standard used to assess the fuels in this investigation.

2.2 Methods

2.2.1 Kinematic viscosity

Viscosities were determined in accordance with ASTM D445. A Canon-Fenske capillary kinematic viscometer was used. Temperature modulation was achieved using a refrigeration unit. Samples within the viscometer were allowed to rest at the required temperature for a minimum of 5 minutes prior to viscosity measurement to allow temperature equilibration. The standard error was found to be no higher than (± 0.067 mm^2s^{-1} at -30 °C, ±0.073 mm^2s^{-1} at -20 °C, ±0.057 mm^2s^{-1} at 0 °C, ±0.128 mm^2s^{-1} at 20 °C and ±0.100 mm^2s^{-1} at 40 °C – more detailed error calculations are available in the supporting information.

2.2.2 Cloud point

Cloud points of the fuels were determined visually by cooling of 1.5 cm^3 vials of the samples in a low temperature freezer, and periodically checking to see if the cloud point had been surpassed. The samples were allowed to rest at each temperature for a minimum of 10 minutes in order to allow equilibration of

sample and freezer temperatures. All cloud points tested were found to have no more than 1 °C standard experimental error.

2.2.3 Distillation

Volatility profiles of all samples were determined in accordance with IP 123. 40 cm^3 of each sample was measured into a 100 cm^3 3 necked round bottom flask with a few PTFE anti-bumping granules. A micro still head/condenser assembly was custom made and contained a number of Vigreux indentations. The samples were heated using a heating mantle and the flask insulated using fiberglass wool to aid vapour rise. Distillate fractions were collected in a graduated measuring cylinder and the liquid and still head temperature recorded at every 5 % increase in distillate fraction. Error of distillate volume measurement was determined to be ±0.5 cm^3. Heating was stopped at a temperature of 300 (±2) °C and distillate recovery recorded. Residue was allowed to cool before removal of the still head/condenser assembly and subsequent weighing to an accuracy of ±0.005 g. The standard error of the distillation was found to be between 2.0 - 7.6% for any given volume, more detailed error is given in the supporting information.

2.2.4 Energy density (Lower calorific value)

Energy content of fuels was determined in accordance with ASTM D3338 through the use of a Parr 1341 plain jacket adiabatic bomb calorimeter using a Parr 1108 oxygen combustion bomb. Approximately 0.3 g of each sample was placed in the crucible within the bomb and the bomb then filled with oxygen to a pressure of approximately 25 bar. The temperature change of the water within the stirred calorimeter was determined to an accuracy of 0.0005 °C. The standard error was found to be between 0.5 – 3% for each of the samples tested.

2.2.5 Flash point

Flash points of each sample were determined in accordance with ASTM D56/IP 170 using a Stanhope-Seta 99880-0 Flashcheck, tag, closed cup flash point machine. All flash point measurements were measured to an accuracy of ±1 °C or less.

2.2.6 Density

Densities were determined via the blending of fuels to the desired composition in a quantity of no less than 40 cm^3 ± 0.1 and weighing to an accuracy of ±0.0001 g multiple times. The error involved in this technique was found to be between 0.6 – 1.2%.

3 Results & Discussion

3.1 Cloud point

The cloud points of the fuels at blend levels of 50% and 20% with Jet A-1 were determined (Fig. 1). The Jet A-1 specification requires that the freezing point must be lower than -47 °C. The majority of fuel blends tested had a suitable cloud point which was found to be between the original freezing point and that of the Jet A-1. However, blends of methyl linolenate and n-butanol clouded above -47 °C while butyl levulinate separated from kerosene at the low temperatures investigated. This demonstrates that while the pure compound might have a suitable freezing point (table 2), molecular interactions with the hydrocarbon fuel can have a negative effect on the solubility of other components. This is a difficult effect to predict, due to the complex nature of the aviation fuel and can really only be determined by experimental testing.

The importance and suitability of the freezing point parameter for aviation fuel specification is not agreed upon ubiquitously however. It has been suggested that the reproducibility of freezing point temperatures is low, with consistency relying heavily of the ability of the operator [24], and that the use of cloud point, cold filter plugging point (CFPP) and pour point temperatures are arguably adequate parameters for the characterisation of low temperature aviation fuel properties [25]. Though other researchers have emphasized that under the current specification the freezing point must be ascertained, also asserting that the CFPP is not relevant to the assessment of a gas turbine fuel [26].

3.2 Viscosity

The Jet A-1 specification stipulates that a fuel must have a viscosity of no more than 8 mm^2s^{-1} at -20 °C. The viscosities of the unblended and blended fuels were ascertained at a range of temperatures from -30 °C up to 40 °C to give a clearer indication of performance (Fig. 2). Highly viscous aviation fuels lead to poor atomisation and combustion, pumping difficulties and in extreme cases the blocking of fuel injectors. All of the blends exhibit ideal-like viscosity behaviour with an approximately exponential increase with a reduction in temperature. n-Hexanol had the highest viscosity of all the alternative fuels tested in this investigation, presumably due to the increased hydrogen bonding between the alcohol groups. As such even at a 20% blend level, n-hexanol lies outside of the required specification. Similarly, n-butanol is also not suitable as an aviation fuel beyond low blend levels. Due to the lack of hydrogen bonding the viscosity of butyl butyrate is more similar to Jet A-1 than either of the alcohols tested. The pure compound was found to be well within the specified minimum at-20 °C while the blends of butyl butyrate are barely distinguishable from Jet A-1 (table 3).

The major source of natural esters is from the transesterification of glycerides. Similarly to butyl butyrate, ethyl octanoate and its blends exhibited a viscosity almost identical to unblended Jet A-1 over the whole temperature range investigated. It is clear that the ability of a molecule to hydrogen bond is undesirable when attempting to replicate the physical characteristics of aviation kerosene. While ethyl octanoate has a low viscosity due to the short chain, methyl linolenate has three double bonds in cis-formation. While this reduces the freezing point to an acceptable level, the interaction of the chain means

that only at low blend levels is the fuel within the required viscosity specification. Butyl levulinate is also more viscous than Jet A-1 and the 50% blend level is only just within the specification.

Despite the level of branching farnesene is extremely viscous and at -20 °C both the 100% and 50% blends are out of specification. Both limonene and ethyl cyclohexane appear to be promising candidates for blending with aviation kerosene. Both fuels have a similar viscosity, which is roughly half that of Jet A-1 at -20 °C. Both fuels blend with aviation kerosene reducing the viscosity of the overall fuel, this could have potentially beneficial consequences in terms of better atomisation and pumping, while also reducing the viscosity of highly viscous aviation fuels.

3.3 Flash point

The flash point of a fuel is the temperature at which an ignitable air/fuel vapour forms above the fuel. Conventional aviation fuel is a complex mixture of a few hundred different hydrocarbons and as such, the molecular interactions that may govern the temperature at which the flash point occurs are difficult to predict. In this investigation the flash points of all the alternative fuels and their blends with Jet A-1 were determined experimentally (table 4).

The flashpoints of the pure samples are all within specification except for ethyl cyclohexane and n-butanol. The flashpoint of the blended fuels appears to be largely dictated by that of the lower flashpoint component. This leads to the flash points for 50% and 20% blends occurring at very similar temperatures due to a flammable fuel air mixture being produced at the lower flashpoint temperature. Despite this effect the flash point of 20% blends of n-butanol and ethyl cyclohexane are still lower than the specified minimum.

3.4 Volatility

The volatility of a fuel dictates the combustion characteristics to a large extent and has further safety implications such as engine relight after flame-out. While a fuel with a low volatility might not ignite readily in the combustion process, an overly volatile fuel suffers from evaporative losses at altitude. Both of these effects lead to reduced fuel efficiency and increased emissions.

Blending a single component into a jet fuel can lead to a large deviation from the boiling curve if there is little interaction with the hydrocarbon compounds as the biofuel will be distilled out at its boiling point (table 5). n-Hexanol does not appear to have a strong interaction with Jet A-1 evidenced by the plateau in temperature at approximately the b.pt of n-hexanol (Fig. 3). Similarly, n-butanol blends have a comparable distillation profile, though the plateau is more marked due to the b.pt of n-butanol being only 118 °C. On removal of all the n-butanol, the curve reverts back to that resembling Jet A-1, suggesting very little interaction or azeotrope formation between the alcohol and the components. This difference in volatility, relative to Jet A-1, means that engines optimised for aviation kerosene will not operate efficiently with these blends. The higher volatility of the alcohols may also mean higher evaporative losses. A plateau,

at approximately 170 °C, is also observed for a 50% blend of butyl butyrate, though the 20% blend has a similar distillation profile to Jet A-1. The 20% blend would presumably not have a significant impact on the operation of the engine.

Butyl levulinate blends exhibit a distillation curve with a much higher similarity to Jet A-1, particularly at a higher blend level. However, in a 50% blend the initial distillate fractions are collected at temperatures very close to the maximum allowed by the specification, presumably due to the high boiling point of butyl levulinate. It is likely that at a blend level of any greater than 50% the 5% distillate fraction would be collected at a temperature exceeding this maximum value. This lower volatility may cause a reduction in combustion quality as vaporisation will not occur as readily.

Ethyl octanoate blends produce a distillation curve very similar to that of Jet A-1, although a plateau at the boiling point of ethyl octanoate is observed. The volatility of ethyl octanoate is well matched to that of the Jet A-1, and there is no indication that there would be any significant difference in combustion characteristics. Alternatively, the polyunsaturated ester methyl linolenate exhibits a distillation curve very unlike that of Jet A-1. At 50% blend level the maximum temperature for the 5% volumetric distillation is exceeded. Only 35% distillate volume is achieved before the maximum allowed boiling temperature, this precludes methyl linolenate from further consideration as an aviation fuel. A volatility that is much too low, as in the case of methyl linolenate blends, will cause inadequate vaporisation in the combustion section of the engine, and as a result poor combustion leading to a loss of efficiency. It is unlikely that any long chain esters, irrespective of their low temperature behaviour would be suitable for aviation.

Similarly the high boiling point of farnesene means that the maximum temperature for the 5% distillate is exceeded and this blend is also out of specification. Farnesene has a reduced oxidative stability and at high temperatures oxidative degradation is observed despite the additional antioxidant present. This results in oxygenates that have an increased boiling point, and only 70% of the fuel mixture was collected by 350 °C. When the level of farnesene is reduced to 20%, the fuel mixture was found to be just within the specifications until 90 vol% of the fuel had been collected. The final 10% was not removed before 350 °C.

The boiling point of ethyl cyclohexane is the lowest out of all the fuels tested, this correlates with the low flash point. Accordingly at 50% blend level the volatility of ethyl cyclohexane is much greater than that of Jet A-1. This is not surprising in correlation with the low flash point, however, it has implications on the viability of ethyl cyclohexane as a drop-in alternative fuel, particularly at higher concentrations. It seems likely that to produce a suitable jet fuel then further substitution of the hydrocarbon ring would be required.

Limonene exhibits a distillation curve very similar to that of Jet A-1, particularly at the lower blend level. At the higher blend level this similarity reduces to an extent, as the limonene is removed from the mixture. At 20% limonene content, the blend exhibits a distillation curve almost identical to that of Jet A-1; suggesting that at this concentration limonene may be used without deleterious effects upon combustion

quality and efficiency. The 95% distillate volume fractions for the blends were collected at a slightly higher temperature than for Jet A-1 suggesting that there may be a small amount of degradation of limonene, which is likely to be a result of the presence of unsaturated C=C bonds, though this effect is minor in comparison to farnesene.

3.5 Density

The Jet A-1 standard stipulates that the density of a fuel must sit within the range 775 - 840 kg m^{-3}. The density of the fuel is important in the operation of aircraft required to fly long distances, or in smaller aircraft where space is limited. In these cases the limiting factor on range is the volume of the fuel tank rather than the maximum structural weight capacity of the airframe. The densities of the fuel follow a roughly linear trend with blend level (Fig. 4). All the pure fuels are denser than Jet A-1, while limonene, ethyl octanoate, butyl butyrate, methyl linolenate and butyl levulinate fall outside of the Jet A-1 standard. An increased density does not have significant safety implications though a combination of the density and energy density influence the range and payload capacity of an aircraft, and therefore have important economic consequences.

3.6 Energy density (Lower calorific value)

The energy density of a potential fuel impacts on the range vs. payload and a high energy density is vital in trying to maximise the passenger and cargo capacity while retaining range. Where weight capacity is the limiting factor, as is the case with most civil aviation flights, it is desirable to have a fuel that produces the most energy per unit mass whereas in applications where range is to be maximised, the volumetric energy content of the fuel is the most important parameter, and a higher volumetric energy content is desirable [27]. The Jet A-1 used in this study was found to have an energy content of 43.521 MJ kg^{-1}. All the hydrocarbon fuels tested in this study have similar gravimetric energy content as Jet A-1 and fall within the standard minimum of 42.8 MJ kg^{-1} (Fig. 5). As expected none of the oxygenates satisfy this criterion. Of the oxygenated fuels, n-hexanol, methyl linolenate and butyl butyrate possessed the highest gravimetric energy content. Due to the increased density of the oxygenated fuels the difference in volumetric energy content is not as pronounced, though only methyl linolenate is comparable to Jet A-1.

3.7 Simplified payload calculations

To illustrate the effect of the changing density and energy density on the range of a specific aircraft a simple calculation, the Breguet range equation, was used (Eq. 1) where V = flight speed (m/s), (L/D) = lift/drag ratio, g = gravitational constant (m/s^2), sfc = specific fuel consumption (mg/Ns), W_i = initial weight and W_f = final weight. To determine the effect of the novel fuels an adaption to the specific fuel consumption must be made, this adapted equation given by Blakey *et. al.* was used for the fuels investigated in this study (Eq. 2) where sfc = specific fuel consumption and LCV = lower calorific value of

kerosene (LCV_{kero}) and alternative fuel (LCV_{alt}) [27]. The payload range was calculated up to the maximum volumetric capacity of the fuel tanks (Fig. 6). The historic data was used for a Boeing 737-300 CFM56-3B1, also given by Blakey et.al.

$$Range = \frac{V(\frac{L}{D})}{g \cdot sfc} ln\left(\frac{W_i}{W_f}\right) \quad (1)$$

$$sfc_{alt} = sfc_{kero}\left(\frac{LCV_{kero}}{LCV_{alt}}\right) \quad (2)$$

The Breguet equation is the simplest flight model and assumes the aircraft is in straight and level flight for the whole flight, that the fuels combust as efficiently as Jet A-1 kerosene and that no structural changes to the plane are necessary to accommodate the novel fuels. Due to all of these assumptions this model normally overestimates the fuel range and is intended to be used as a method of comparison between the fuels rather than an accurate depiction of the range of an operating aircraft. To simplify the assessment the equation was used up to the volumetric limit of the fuel. The flat portion of the graph at approximately 16,000 kg payload is the range at the maximum payload capacity of the aircraft. The range at maximum payload increases as more fuel is added. The first change in payload corresponds to the point at which the maximum structural weight of the airframe is reached, after which as more fuel is added to increase range, payload must be decreased by removal of cargo or passengers in order to accommodate the weight of the new fuel.

All the hydrocarbon fuels tested have similar or better performance than the Jet A-1 used in this study and from a range vs. payload perspective actually improve on the current technology. Both ethyl cyclohexane and farnesene have a lower density than limonene, meaning that the volume capacity of the fuel tanks is reached at a lower mass of fuel. All the oxygenated fuels have a reduced maximum range, except for methyl linolenate which is comparable to Jet A-1, though the maximum payload at this range is severely reduced. While the energy density is substantially lower, the density of methyl linolenate is very high (895 kg m^{-3}) giving a better volumetric performance. n-Hexanol has a similar range to methyl linolenate but as it has a far lower density the maximum range is reduced substantially. As the oxygen content increases the range of the fuel is decreased, as shown by the poor range vs payload of n-butanol and butyl butyrate. Butyl levulinate has the worst performance of the fuels under investigation. While methyl linolenate had a comparable range to Jet A-1, though at the cost of a low payload, few of the other properties were within specification for aviation. If biodiesel is to be adopted as an aviation fuel then short chain esters over polyunsaturated chains are necessary, however, ethyl octanoate has a low energy density and therefore a poor range against payload.

4. Conclusions

The characterisation of the physical properties of a range of potential aviation biofuels and their blends was undertaken. The viscosity of n-hexanol even at low blend levels was too great to be compatible with aviation kerosene, this was also found to be the case for n-butanol. Both alcohols also distilled out of the kerosene fuel at low temperatures, which would affect the performance substantially. In addition the cloud point and flash point of n-butanol blends were out of specification. A better alternative was found to be butyl butyrate which has a higher boiling point than the alcohols and therefore had a more similar distillation profile to Jet A-1. The viscosity, flash point and low temperature behaviour were also similar to Jet A-1, though the reduced energy density meant that a maximum range of an aircraft would be approximately 85% that of Jet A-1. This range was reduced even further on using butyl levulinate and though in all other respects this seemed a reasonable substitute for aviation kerosene it is not miscible at low temperatures.

FAAE have also been suggested as alternatives for aviation, however, to permit the requisite low temperature behaviour they must primarily be either short chain esters or highly polyunsaturated. In this study ethyl octanoate, a C_8 ester, was demonstrated to have remarkably similar properties to Jet A-1. The pure ester and all blends tested were fully within the Jet A-1 specification except for the lower calorific value. Alternatively methyl linolenate, a C_{18} ester with three double bonds, has a greatly increased energy density and the maximum range of an aircraft would likely be similar to Jet A-1. However, methyl linolenate is not volatile enough, too viscous and when blended has too high a cloud point to be considered as an aviation fuel substitute. It is clear that if biodiesel is to be used for aviation then it will have to contain short chain esters rather than long chain polyunsaturates.

Three hydrocarbon fuels, farnesene, ethyl cyclohexane and limonene, were also examined. All three fuels had excellent energy density and would potentially match range vs. payload performance of Jet A-1. However, farnesene was shown to be too viscous for use as an aviation fuel and is presumably too oxidatively unstable. Ethyl cyclohexane, on the other hand, is too volatile and has too low a flash point. Alternatively, limonene was found to be an excellent substitute for aviation kerosene and, potentially with additional antioxidants, could be used as a drop in replacement biofuel requiring no further chemical upgrading.

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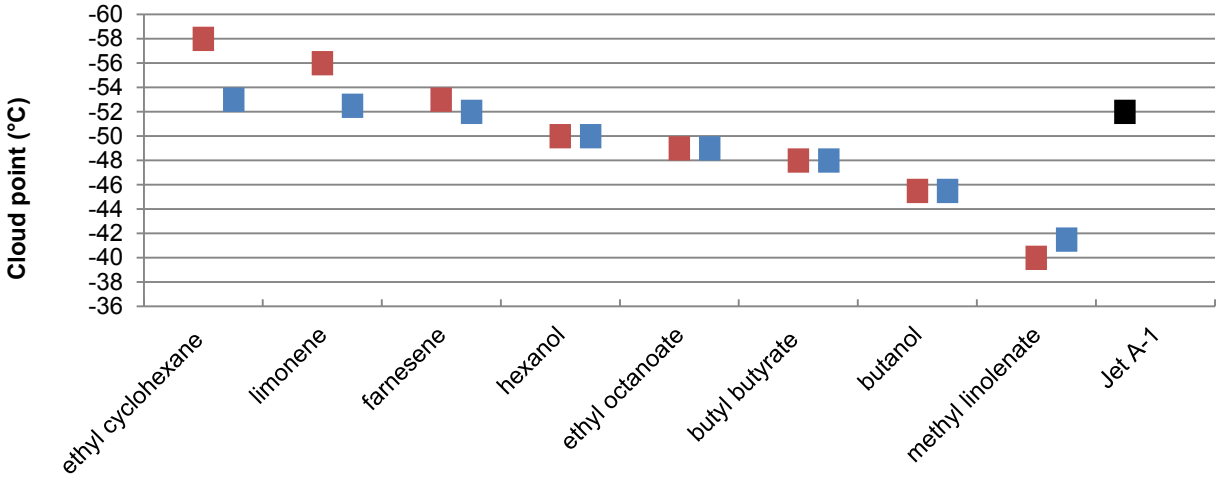

Fig. 1. Cloud points measured for 50% and 20% fuel blends. The maximum freezing point in the Jet A-1 standard is -47 °C.

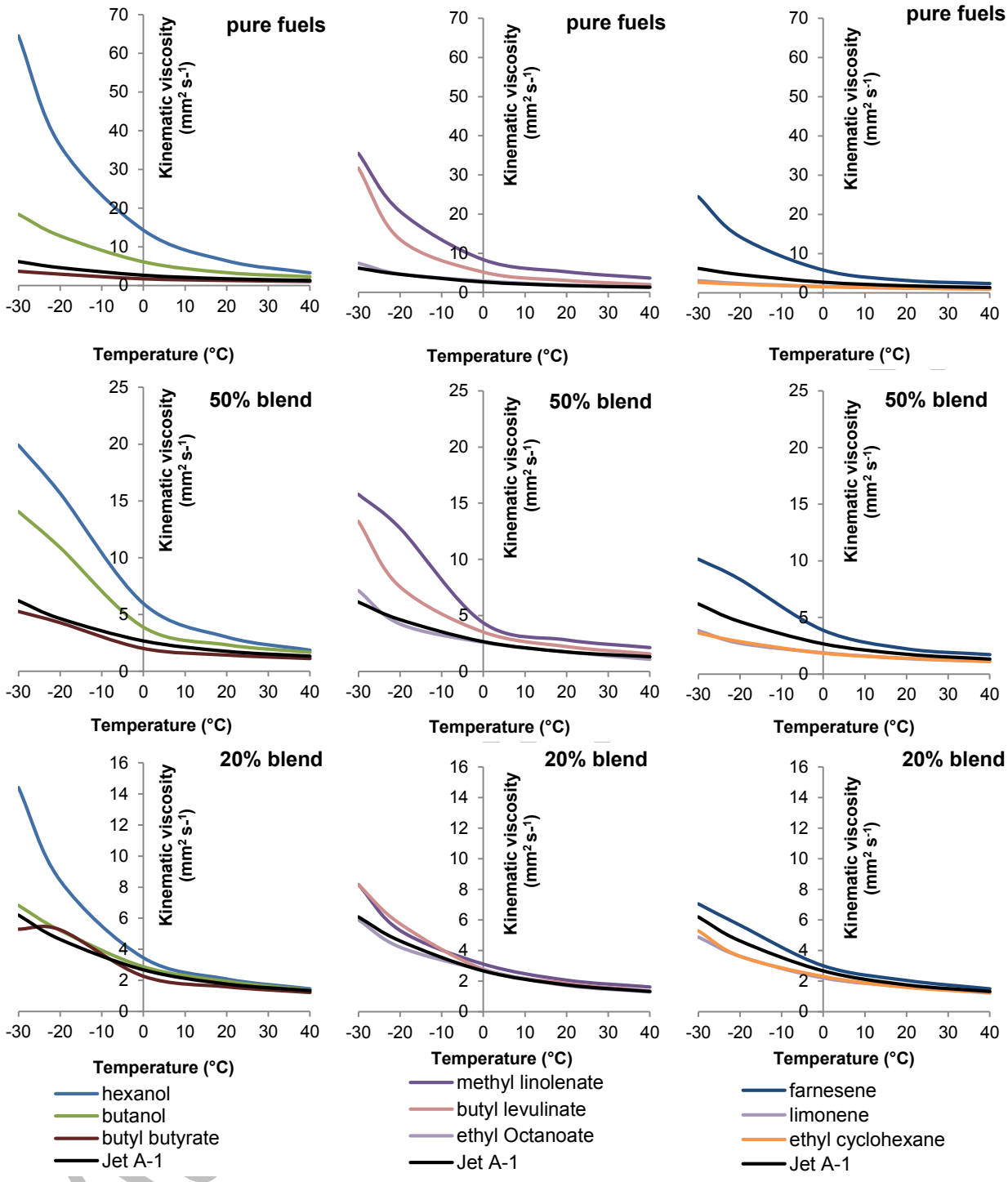

Fig. 2. Smoothed curves showing the kinematic viscosity for the pure fuels, 50% and 20% blends over the temperature range -30 – 40 °C, measurements were taken at -30 °C, -20 °C, 0 °C, 20 °C and 40 °C. The full data set is available in the supporting information.

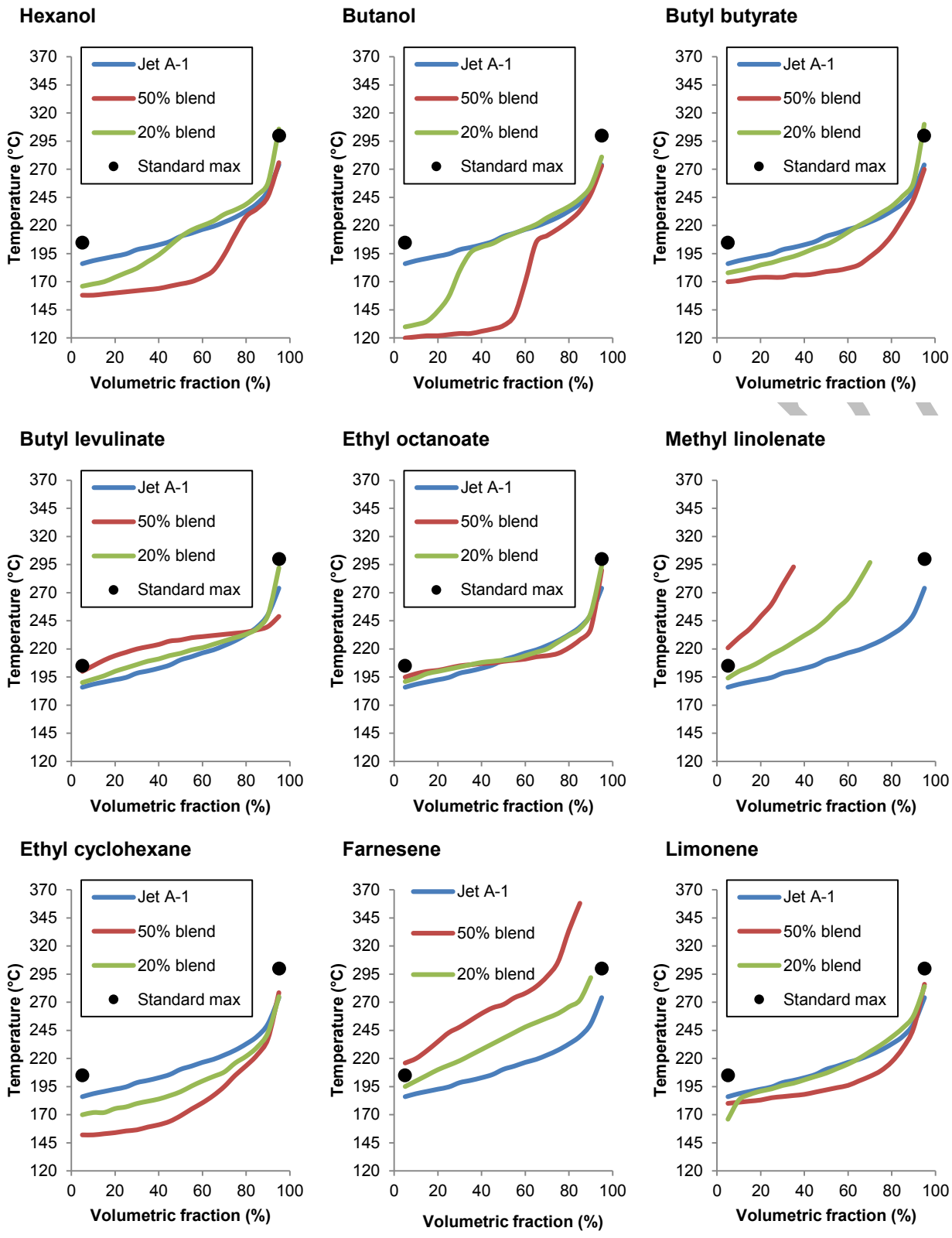

Fig. 3. Boiling curves for the alternative aviation fuel blends, the black circles show the maximum temperature allowable for a given mass fraction

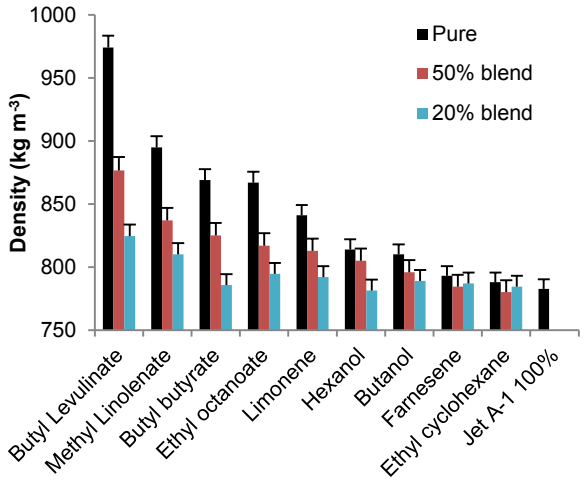

Fig. 4. Densities of the pure fuels, 50% and 20% blends with Jet A-1 at 15 °C, in comparison the minimum and maximum density set out in the Jet A-1 standard is 775 kg m^{-3} and 840 kg m^{-3} respectively.

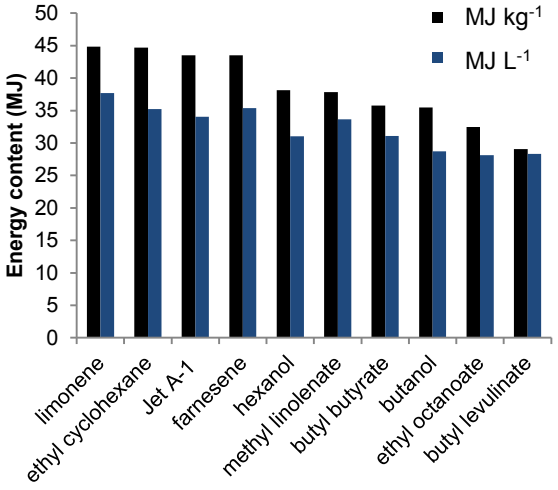

Fig. 5. Energy densities of the pure fuels examined in this study, the minimum energy density set out in the Jet A-1 standard is 42.8 MJ kg^{-1}

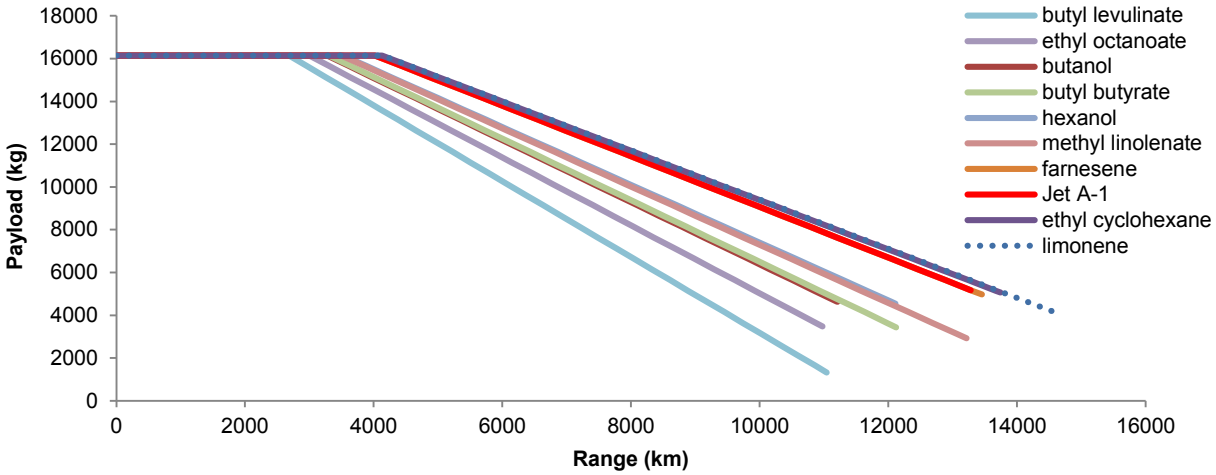

Fig. 6. Simplified payload calculations, using an adapted Breguet equation given by Blakey *et. al.* for the range of pure fuels investigated over the course of this study [27].